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RESEARCH ON KINETICS OF SYNTHESIS OF HYDRAZINE

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WRIGHT AIR DEVELOPMENT CENTER

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Midwest Research Institute

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FOREWORD

This is the final report issued by the Midwest Research Institute, describing work performed under Contract AF 33(616)-2043. The RDO number is 478-333, entitled "Kinetics of Synthesis of Hydrazine." It covers the period of 15 April 1953 to 30 April 1954. The investigator is Jack D. Bush, and the contract was monitored for WADC by the Aeronautical Research Laboratory with Jean T. Dubois acting as the project engineer.

ABSTRACT

Hydrazine is recognized as a high-energy fuel with excellent physical properties. Its potential usefulness in national defense has led to studies of alternative ways of producing it. One such study was directed toward identification of a catalyst which would convert ammonia and nitrous oxide to hydrazine. A number of relatively inert catalysts were found to convert around 0.1 per cent of the reacting nitrous oxide to hydrazine in simple laboratory equipment. Yields of this magnitude were obviously unsatisfactory, and the identification search was abandoned.

A consideration of the limited knowledge of and some plausible assumptions about kinetic relationships revealed a small but real possibility that a satisfactory conversion of nitrous oxide and ammonia to hydrazine might be obtained under suitable conditions. These conditions were presumed to be (a) higher reaction temperature associated with shorter reaction time and (b) higher partial pressure of ammonia. The laboratory procedure involved preheating the reagent gases separately, mixing them, passing the mixture at atmospheric pressure through a catalyst bed, and quenching the product mixture as rapidly as possible. It was thought that better results might be obtained in a "diesel engine" reactor. Operation of that reactor would involve passage of a mixture of reagents at a moderate temperature into a cylinder, compression of the mixture to attain a higher ammonia pressure and a quick rise to the desired reaction temperature, and expansion to quench the mixture quickly. The preparation and maintenance of a satisfactory catalyst bed was a recognized difficulty.

Direct proof of the usefulness of a diesel engine reactor appeared to involve expensive equipment and a prolonged development program. The postulates, which indicated that usefulness, could be subjected to test in laboratory equipment of the type already used. The present project was set up to provide experimental support for those postulates. A preheater, reaction chamber, and quencher were constructed from Vycor, heating coils, and insulation. Acetone which had been cooled by dry ice was circulated through the quencher. The quencher and a subsequent condenser removed ammonia, water, and hydrazine from the product stream. The ammonia was vaporized, and the hydrazine content of the residual water was measured by titration with standard iodate.

Experimental studies covered the following conditions: 500° to 800°C, 5:1 to 30:1 ammonia:nitrous oxide ratios, 0.46 to 10.7 liters of reagent gas per minute, 20 to 0 cc of quartz or Vycor catalyst. The improvement of hydrazine yield by increase in reaction temperature and decrease in reaction time was demonstrated. Rate of formation of hydrazine and rate of reduction of nitrous oxide were both shown to be nearly zero order with

respect to nitrous oxide concentration. A maximum conversion of 0.85% of the reacting nitrous oxide to hydrazine was obtained at 750°C under conditions which caused reduction of about 1.8% of the input nitrous oxide.

Conditions which might lead to 50% conversion of input nitrous oxide to hydrazine were described. The specifications which a diesel engine reactor would have to meet were listed. The cost of production of hydrazine by use of such a device was estimated at about $0.60 per pound. Since the production cost by the Raschig process is about $0.30 per pound, development of a diesel engine reactor cannot be justified by simple economics. The importance of the fact that this process requires no chlorine cannot be estimated.

PUBLICATION REVIEW

The publication of this report does not constitute approval by the Air Force of the findings or the conclusions contained therein. It is published only for the exchange and stimulation of ideas.

FOR THE COMMANDER:

LESLIE B. WILLIAMS, Colonel, USAF
Chief, Aeronautical Research Laboratory
Directorate of Research

I. INTRODUCTION

This project was set up to measure kinetic relationships in the oxidation of ammonia by nitrous oxide. It is intended to show whether conditions exist such that hydrazine can be obtained as the major part of that reaction and to indicate whether such conditions, if found, might be practical for industrial production of hydrazine.

Equipment, experimental techniques, and results of initial synthesis experiments were described in previous reports. This report quotes results of further synthesis experiments and discusses the kinetic relationships thus indicated. A proposed process is described and a preliminary estimate of operating costs is offered. The limited promise of further investigation of this reaction is discussed.

II. EXPERIMENTAL WORK

Equipment

The assembly for study of reaction kinetics consisted of supplies of nitrous oxide and ammonia, flow control equipment, a specially constructed combination of preheater, reaction chamber, and quencher, and equipment for collection and analysis of samples. Details of design were given in earlier reports.

One relatively minor change was made late in the program. The original quencher was found inadequate for high reaction temperatures and high flow rates. A simple U-tube was made from 6-mm Pyrex tubing and ball joints and inserted between the original quencher and the sample-collection assembly. A dry ice - acetone bath around this U-tube provided enough supplemental cooling for effective condensate of most of the ammonia in the spent gases from the reactor.

Hydrazine Production

Initial results of hydrazine synthesis experiments were quoted in Table I of Progress Report No. 3. Table I of this report lists results of further experiments in the same manner. Data for individual experiments include rates of input of ammonia and nitrous oxide in liters per minute, reaction temperatures in °C, the volume, in milliliters, of residual gas after

TABLE I

HYDRAZINE FORMATION ON FUSED QUARTZ

Date	Feed Rates liter/min NH₃	N₂O	Reaction Temp. °C	Gas Res. ml	Length of Run min	Liquid Volumes NH₃	H₂O	IO₃	Hydrazine Yield % of NNO In	to Gas	to H₂O
			20 cc, 20.33 gm, 25-35 mesh quartz								
1/11/54	3.03	0.130	513	7.0	152	475	0.4	0.0	--		--
1/12/54	2.96	0.130	549	10.2	60	195	0.35	0.5	0.0024		0.03
1/12/54	2.96	0.130	560	10.8	60	190	0.40	0.6	0.0029		0.03
1/13/54	2.96	0.032	560	35.0	60	125	0.25	x	--		--
1/14/54	1.25	0.046	501	11.7	193	280	0.5	x	--		--
1/14/54	0.45	0.010	501	27.0	270	>40	0.2	x	--		--
1/15/54	1.20	0.044	551	23.0	172	240	0.95	x	--		--
			4 cc, 4.12 gm, 25-35 mesh quartz								
1/20/54	3.15	0.138	555	--	90	285	0.15	0.7	0.0028		0.10
1/21/54	1.20	0.062	546	--	120	145	0.20	0.1	0.0005		0.01
1/21/54	1.20	0.060	544	--	60	85	0.10	0.1	0.0011		0.02
1/26/54	1.20	0.058	548	--	180	235	0.25	x	--		--
2/2/54	1.15	0.050	598	--	183	250	0.4	1.1	0.0046		0.06
2/3/54	3.03	0.140	595	10.0	90	255	0.2	2.8	0.0085		0.29
2/3/54	3.03	0.140	602	6.0	85	255	0.15	2.9	0.0093		0.40
			23.24 gm, 10-12 Vycor								
2/8/54	3.03	0.142	602	18.0	90	280	0.8	1.2	0.0036		0.03
2/8/54	2.96	0.140	595	18.3	60	180	0.6	1.5	0.0048		0.03
			11.8 gm, 10-12 Vycor								
--	1.20	0.046	605	76.5	60	85	0.9	x	--		--
3/2/54	3.03	0.137	602	9.8	93	300	0.6	0.5	0.0015		0.02
3/5/54	6.0	--	593	7.1	19	220	0.2	0.3	--		0.03
3/5/54	3.03	0.131	621	14.5	93	290	0.8	1.5	0.0047		0.04
3/5/54	0.8	0.0232	626	40.0	30	75	1.0	0.3	0.0165		0.006

TABLE I (Concluded)

Date	Feed Rates Liter/min NH₃	N₂O	Reaction Temp. °C	Gas Res. ml	Length of Run min	Liquid Volumes NH₃	H₂O	I₂O₃	Hydrazine Yield % of NNO In	to Gas	to H₂O
					11.8 gm, 10-12 mesh Vycor (concluded)						
3/11/54	2.8	0.136	697	13.0	90	265	1.0	7.1	0.022		0.18
	0.8	0.0134	694	39.5	120	90	2.5	0.9	0.0021		0.007
3/12/54	7.2	1.12	720	8.0	29	205	1.8	19.6	0.023		0.22
	7.0	0.56	720	9.0	44	340	1.6	21.5	0.033		0.28
	7.0	0.24	711	--	45	335	1.6	12.3	0.043		0.16
3/30/54	7.2	0.28	800	25.5	36	255	2.0	19.5	0.075		0.20
	6.8	0.81	810	17.5	24	170	1.7	19.5	0.038		0.23
3/31/54	6.7	1.70	786	--	12	80	0.4	6.1	0.0113		0.31
	9.0	0.27	754	30.5	30	285	1.4	5.6	0.026		0.08
	8.9	0.81	752	13.5	30	285	1.5	9.2	0.015		0.13
	8.8	0.79	748	15.0	30	270	1.5	16.7	0.027		0.23
	8.7	0.79	766	15.2	30	270	1.4	13.0	0.021		0.19
	8.8	1.70	752	6.0	30	255	0.9	20.8	0.0156		0.47
4/1/54	9.0	1.73	730	5.5	30	270	0.7	14.0	0.0103		0.41
	8.9	1.74	740	--	30	260	0.6	12.9	0.0094		0.44
	8.8	1.72	744	6.0	30	260	0.8	15.8	0.0113		0.40
	8.8	1.72	756	6.0	30.3	262	0.5	13.8	0.0102		0.56
4/5/54	9.0	1.69	697	--	50.5	480	1.2	23.3	0.0104		0.40
	8.9	1.69	725	--	40	380	1.1	23.5	0.0133		0.44
	8.9	1.70	752	--	30	270	0.8	21.4	0.0161		0.55
	8.1	1.69	740	--	50	450	0.9	24.0	0.0109		0.55
				1.63 gm, 10-12 mesh Vycor							
4/6/54	8.3	1.60	752	--	40	348	0.7	26.1	0.015		0.76
	8.2	1.60	807	--	30	261	1.3	33.5	0.027		0.53
				No catalyst							
4/7/54	8.0	1.68	749	--	80	710	1.3	53.8	0.015		0.35
	8.0	1.68	807	--	32	260	1.1	29.5	0.021		0.55

scrubbing a 100-milliliter sample of uncondensable product gas with 1.5 liters of water, the duration of each run in minutes, the volume of condensate as milliliters of liquid ammonia, the volume of residual liquid after evaporation of ammonia as milliliters of water, the volume in milliliters of standard iodate solution required to oxidize the hydrazine in the residual liquor, and the hydrazine yield as percentage of nitrous oxide specified in three different ways: (1) nitrous oxide supplied to the reactor, (2) the nitrous oxide which reacted to yield non-condensable gases, and (3) the nitrous oxide which reacted to yield residual water.

Previously reported results were obtained exclusively with a 20-milliliter reaction chamber filled with Vycor, crushed and screened to 25-35 mesh. Initial experiments at temperatures near 800° and 700°C gave no measurable yields of hydrazine. Experiments at temperatures near 600°C had shown that results of duplicate experiments usually agreed within a factor of two. Decreasing the nitrous oxide concentration in the reaction mixture had failed to improve the percentage conversion to hydrazine in the expected manner.

Table I of this report shows results for several different catalyst charges and for temperatures ranging from 500° to 800°C. Objectives and significances are discussed below.

One thesis under test stated that optimum hydrazine yield should increase with increase in reaction temperature. After proof of yields at 600°C had been obtained, the thesis received substantial support from a lack of measurable hydrazine yields at 500°C and very modest yields at 550°C. Measurements of residual water and residual noncondensable gas demonstrated reaction of some 10 to 30% of the input nitrous oxide. Hence, the lack of yield at 500°C was shown to be due to an unfavorable mechanism rather than to either complete reaction or complete inertness of reagents. It had already been demonstrated that pressure drop through the catalyst bed prevented higher flow rates than the quoted 3+ liters per minute and that consumption of nitrous oxide at that flow rate and 700°C was virtually complete; hence, no yield of hydrazine at higher temperatures could be obtained from the initial catalyst bed.

A second thesis stated that a decrease in the percentage of nitrous oxide reacting to form water should be accompanied by an increase of the percentage of the reacting hydrazine nitrous oxide recovered as hydrazine. The catalyst bed was reduced from 20 to 4 milliliters of 25-35 mesh crushed Vycor and further runs were made at 550° and 600°C. The hydrazine concentration in product water increased by a factor of about 3, indicating the possibility of a further limited increase in conversion of reagents to hydrazine.

The two ways of cutting down the extent of reaction were reduction of catalyst surface and increase in flow rates of reagents. Decrease in volume of catalyst was objectionable because there was no satisfactory provision for measurement of the temperature directly on the catalyst support disc. The chamber was filled with 23.24 gm of 10-12 mesh Vycor (about 20 milliliters bulk volume). This charge induced more formation of water and uncondensable gas than the one it displaced. The catalyst charge was cut to 11.8 gm. Initial experiments at 600°C showed that decrease in flow rates of reagents increased the hydrazine yield per amount of input nitrous oxide, but decreased the yield per amount of reacting nitrous oxide. The new bed allowed the maximum flow rate of reagent gas to be doubled.

A third thesis stated that the percentage conversion of nitrous oxide to hydrazine should increase with decrease in output hydrazine concentration; therefore, also with decrease in initial nitrous oxide concentration. Experiments at 700°, 800°, and 750°C definitely contradicted the thesis concerning initial nitrous oxide concentration. It appears that there is an optimum nitrous oxide concentration and that that optimum concentration may increase with temperature. Water formation seems to be nearly independent of nitrous oxide concentration and hydrazine formation is definitely less than first order with respect to that reagent.

The lack of adequate means for temperature measurement at the catalyst support disc led to a set of runs in which all operating variables were kept constant except the voltage to Heater No. 6 (cf. Fig. 1, Progress Report No. 3). Within the limits of error, the setting of this heater had no decisive influence on hydrazine yield.

Previous results showed better conversion of reacting nitrous oxide to hydrazine at 750°C than at either 700° or 800°C. Within the limits of error, the optimum reaction temperature appeared to lie in the immediate neighborhood of 750°C.

The recent experiments showed that limitations of the reactor assembly were becoming important. An ammonia stream of 9 liters per minute could not be much above 800°C without replacing Heaters Nos. 2 and 3. On the other hand, the quencher at hand was loaded to capacity when cooling product gases to room temperature for that rate and temperature. The extra cooling capacity was provided as previously described, but the delayed cooling was recognized as an implication of loss of hydrazine.
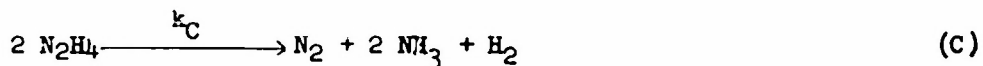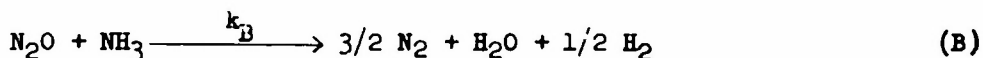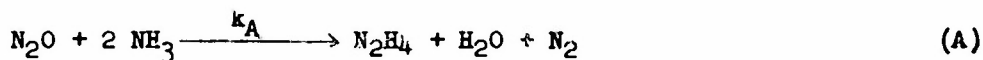
Further efforts to increase conversion of nitrous oxide to hydrazine were made. First the catalyst charge was decreased from 11.8 to 1.63 gm. The five-fold reduction in catalyst failed to double the conversion. Then

the loose catalyst was removed completely. Only the catalyst support disc remained. This allowed a slight increase in conversion.

III. DISCUSSION OF RESULTS

It was originally intended that this project should provide a comprehensive demonstration of a generalized reaction mechanism and should identify the most favorable of a series of catalysts. Not all the initial objectives were reached. No effective study of activities of different catalysts was made. The kinetics study permitted few definite conclusions about reaction mechanisms. However, some ideas which were originally mere speculations are now supported by experimental results.

The proposal listed three reactions and indicated some assumptions that might be drawn regarding reaction kinetics. These are quoted as follows:

$$N_2O + 2\ NH_3 \xrightarrow{k_A} N_2H_4 + H_2O + N_2 \tag{A}$$

$$N_2O + NH_3 \xrightarrow{k_B} 3/2\ N_2 + H_2O + 1/2\ H_2 \tag{B}$$

$$2\ N_2H_4 \xrightarrow{k_C} N_2 + 2\ NH_3 + H_2 \tag{C}$$

$$\frac{dP_{N_2O}}{dt} = -k_A \cdot P_{N_2O} \cdot P_{NH_3}^2 - k_B \cdot P_{N_2O} \cdot P_{NH_3} \tag{D}$$

$$\frac{dP_{N_2H_4}}{dt} = +k_A \cdot P_{N_2O} \cdot P_{NH_3}^2 - k_C \cdot P_{N_2H_4}^2 \tag{E}$$

Equation A is the only stoichiometric relationship to be expected between amounts of reagents and amount of the desired hydrazine. Equation B is the simplest but not the only relationship between reagents and possible by-products which does not involve hydrazine. No study of the question of preferential oxidation of ammonia or hydrogen has been made. Equation C is also one of several possible stoichiometric relationships between the desired hydrazine and possible decomposition products. Equations D and E are highly speculative kinetic relationships based upon the assumptions that Reactions A, B, and C have kinetic as well as stoichiometric significance.

The thesis that that percentage conversion of nitrous oxide
to hydrazine should increase with decrease in original nitrou. oxide con-
centration is a combination of two arguments. The first is that hydrazine
decomposition is higher than first order with respect to hydrazine. The
second is that the rate of formation of hydrazine depends upon the nitrous
oxide concentration; therefore, under otherwise fixed conditions, increase
in nitrous oxide concentration should increase the hydrazine concentration
in product gases. High-order hydrazine decomposition is known to occur on
some materials. However, the present project demonstrates that rate of
synthesis of hydrazine is nearly independent of the nitrous oxide concentra-
tion. The synthesis mechanism is evidently complicated, and the nitrous
oxide apparently reacts not with ammonia as such, but with transient inter-
mediates. Possible reaction with one intermediate leads to hydrazine forma-
tion, whereas another intermediate must be oxidized to keep it from destroy-
ing hydrazine. If that is true, it appears that increase in temperature
favors development of the latter intermediate more than the former, thus
accounting for the increase in optimum nitrous oxide content with temperature.

The thesis that a decrease in the percentage of nitrous oxide
reacting to form water should be accompanied by an increase in the percentage
conversion of reacting nitrous oxide to hydrazine is based upon the qualita-
tive idea underlying Eq. E. It is assumed that hydrazine is an unstable in-
termediate in a series of consecutive reactions. The concentration of that
intermediate increases rapidly when the preheated reagents mix and enter the
reaction zone. As that concentration rises, the rate of destruction of the
intermediate also rises until a balance point is reached. Thereafter, the
rates of formation and destruction of the intermediate are virtually equal,
and the concentration of the intermediate gradually decreases with decrease
in concentrations of the reagents.

It was originally presumed that hydrazine formation is first order
with respect to nitrous oxide and second order with respect to ammonia,
whereas hydrazine decomposition is second order with respect to hydrazine.
Results of this program show that hydrazine formation is less than first
order with regard to nitrous oxide. If the small effect of nitrous oxide
concentration is neglected, it appears that the balancing ratio of hydrazine
concentration to ammonia concentration is near 10^{-5}; that is, k_C is about
10^5 times k_A .

As a general rule, high values of specific rate constants are as-
sociated with low activation energies. Therefore, an increase in temperature
usually reduces the difference between rates. However, in the present case
there is little indication that rise in temperature favors hydrazine formation
more than hydrazine decomposition.

The thesis that optimum hydrazine yield should increase with increase in reaction temperature is based on a combination of ideas. First, if the contact of reagents with catalysts is sufficiently limited, the hydrazine concentration actually developed is also limited and hydrazine destruction is negligible. Under such circumstances the ratio of product hydrazine to product water becomes a measurement of the ratio $k_A:k_B$ of the specific rate constants in Eq. D. Again, an increase in temperature should bring this ratio closer to unity. It appears that reaction rates are so rapid that hydrazine decomposition cannot be effectively suppressed at 800°C with the present reactor. The effect of nitrous oxide concentration is known to be negligible. The assumption of different effects of ammonia concentration on formation of hydrazine and destruction of nitrous oxide is plausible but not established; hence, the exact significance of k_A and k_B cannot be stated. It is clear that the limiting ratio of hydrazine formation to nitrous oxide reduction increases with temperature but the manner of increase is somewhat obscure. Comparison of the absence of measurable hydrazine at 500°C with the maximum yield at 750°C would indicate a great advantage of increase in temperature. Comparison of the maximum yield at 600°C with that at 750°C indicates a very modest advantage. In view of the lesser ratio of water to condensed ammonia for values at 600°C, the measured yield ratio at that temperature appears to be somewhat closer to its limit than is the value at 750°C. If it is assumed that the ratio increases by a factor of 5 for each 100° rise in reaction temperature, and that the maximum ratio at 750°C is 1%, the maximum ratio at 1000°C would be about 50%. On the other hand, the increase in all reaction rates, including rate of decomposition of hydrazine, forces the use of shorter periods of contact of reagents with catalysts. The passage of 10 liters of gas per minute through a 10-cc catalyst bed at 750°C allows significant decomposition of hydrazine. This involves a contact time of only 0.06 second. At 1000°C the contact time might be cut to the order of 0.001 second. This length of reaction period is typical of an explosion rather than a conventional reaction. The high temperature and short reaction time appear to be beyond not only the present reactor but any reactor of that general pattern. Even though there is a real possibility of satisfactory conversion of reagents to hydrazine, there is no hope that the postulated drastic quench and the yield of less than 1% per cycle of reagent gases could be expanded into a large-scale process.

An alternative procedure for rapid heating and cooling of gases is known. When a mass of gas is compressed adiabatically its temperature rises; when the gas expands its temperature falls. Therefore, the hydrazine synthesis reaction might be carried out in something analogous to a diesel engine. The capabilities of such a device are considered in connection with Fig. 1.

It is assumed that the effective reaction time for a gas mixture within a diesel engine cylinder is limited to that period in which the cylinder is within 15° of top dead center. Then a reaction time of 0.001 second re-

Fig. 1 - Proposed Setup for Hydrazine Synthesis.
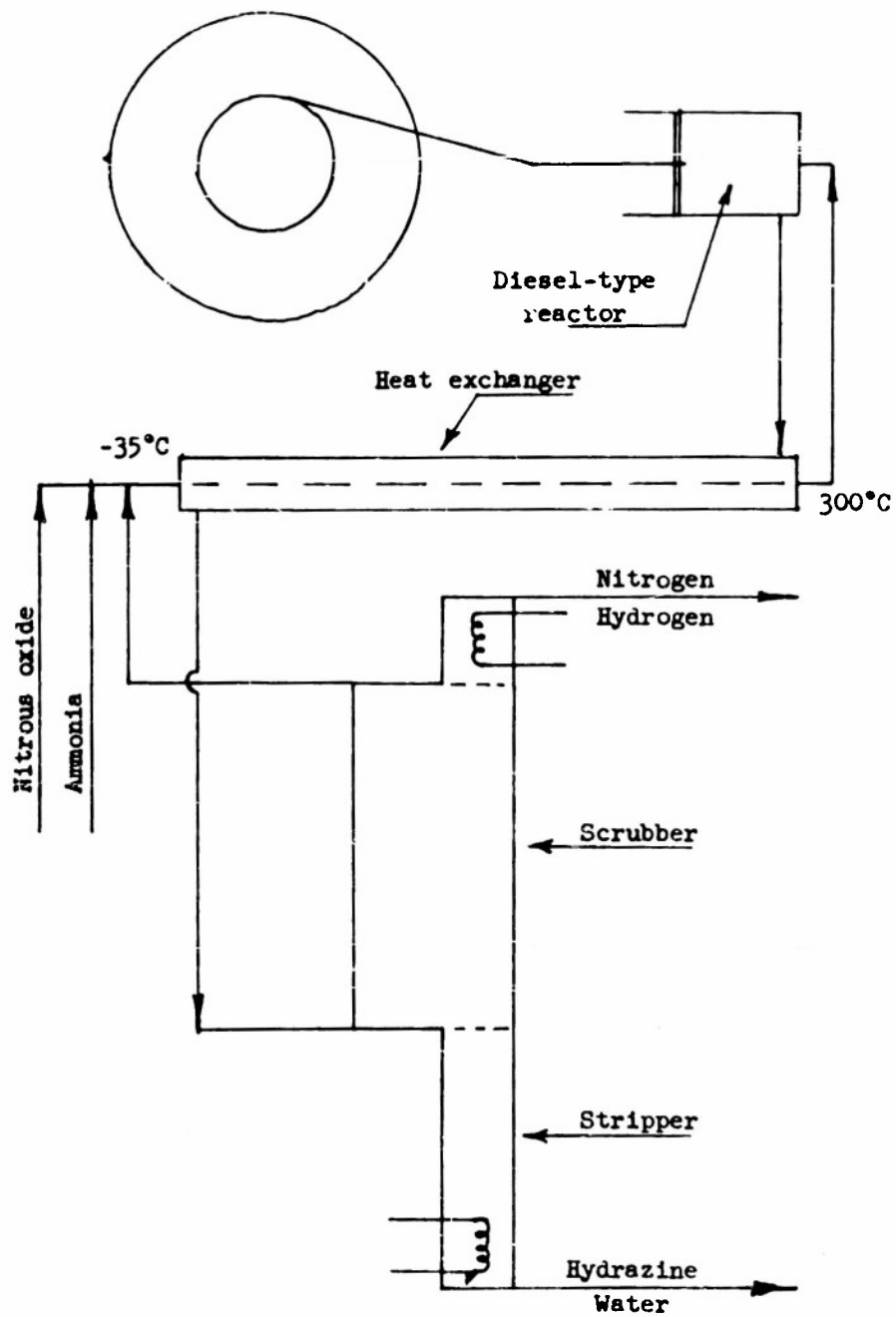
quires an engine speed of 5000 revolutions per minute -- high, but possible.
The maximum practical ratio of high pressure to low pressure is about 20:1.
The corresponding temperature ratio is about 2.35:1 ; hence, gases heated
to 1000°C when fully compressed would emerge from the engine at a tempera-
ture near 300°C. This is low enough to permit further cooling in heat
exchangers without undue loss of hydrazine on exchanger surfaces. The gases
could then be cooled to the dew point of the ammonia therein, and passed
through a scrubbing tower. A ratio of 50 moles of vapor to 1 mole of liquid
would permit removal of all water and presumably all hydrazine. A portion
of the vapor would be withdrawn to the condenser to provide most of the liquid
ammonia condensate, then further treated to recover nitrous oxide and ammonia
from non-condensable waste gas. The major part would be passed back through
the heat exchanger, mixed with makeup reagents, and recycled through the
engine. A hydrazine-water mixture could be recovered from a relatively small
stripping section below the scrubber.

A preliminary cost estimate is offered on the basis of the follow-
ing assumptions: (a) 50% of the stoichiometric amount of hydrazine is re-
covered, (b) the maximum hydrazine concentration of gas leaving the engine
is 0.2 mole per cent. The high compression ratio involves a high friction
loss in the engine; also, the limited extent of the combustion of reagent
gases delivers very little energy. Outside power requirements should cost
about $0.15 per pound of hydrazine. Depreciation cost should be about $0.10
per pound. If the scrubbing operation is carried out at atmospheric pressure,
refrigeration costs should be about $0.05 per pound. Ammonia costs less than
$0.05 per pound. It may be possible to produce nitrous oxide economically
by catalytic oxidation of ammonia. Since only half the ammonia in the above
reactor goes to hydrazine, reagent costs of $0.10 for ammonia and $0.20 for
nitrous oxide per pound of hydrazine are specified. Total costs for this
process then amount to about $0.60 per pound.

It seems that actual production costs for full-scale production of
hydrazine by the Raschig process amount to only about $0.30 per pound. In
spite of various optimistic assumptions about processing difficulties, the
combustion-type process outlined above does not offer any economic advantages.
However, if it is feasible as presumed, its cost is not completely prohibi-
tive, and elimination of the need for chlorine may be sufficiently important
to justify experimental study.

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